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Control Technology Assessment Report for Air Emissions from Wastewater Treatment Operations

Research Triangle Inst., Research Triangle Park, NC

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Abstract: Air emissions from the wastewater treatment operations at a chemical manufacturing plant were investigated at the request of a State air pollution control agency. The report presents information on existing emission controls and options for additional controls, with associated costs.

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CONTROL TECHNOLOGY ASSESSMENT REPORT

FOR AIR EMISSIONS FROM

WASTEWATER TREATMENT OPERATIONS

CONTROL TECHNOLOGY CENTER

SPONSORED BY:

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Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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WASTEWATER TREATMENT OPERATIONS

by

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PREFACE

This investigation of air emissions from wastewater treatment operations was funded as a project of EPA's Control Technology Center (CTC).

The CTC was established by EPA's Office of Research and Development (ORD) and Office of Air Quality Planning and Standards (OAQPS) to provide technical assistance to State and local air pollution control agencies. Three levels of assistance can be accessed through the CTC. First, a CTC HOTLINE has been established to provide telephone assistance on matters relating to air pollution control technology. Second, more in-depth engineering assistance can be provided when appropriate. Third, the CTC can provide technical guidance through publication of technical guidance documents, development of personal computer software, and presentation of workshops on control technology matters.

This investigation was performed at the request of the West Virginia Air Pollution Control Commission. The report examines air emissions from wastewater treatment operations at a chemical manufacturing plant. The report presents information on existing emission controls and options for additional controls, with associated costs.

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1.0 INTRODUCTION

The Occidental Chemical Plant at Belle, West Virginia produces C_1-chlorinated solvents (e.g., methylene chloride, carbon tetrachloride, and chloroform). The wastewater generated at this plant is treated in organics/solids decanters and a steam stripper to recover volatile organics before discharge. These operations result in substantial air emissions with high concentration of volatile organics. This report identifies and evaluates various options available to control the air emissions of volatile organics (VOCs). The information gathered in field visits by Research Triangle Institute personnel in September 1986[1] and July 1988[2] is used to estimate the total annual emissions of the VOCs as well as the maximum rate of emissions due to working losses from the wastewater treatment operations. Condensation of organics in a refrigeration system, carbon adsorption and a combination of both techniques are evaluated in this report as possible control options.

2.0 PROCESS DESCRIPTION

The wastewater at the Occidental Chemical plant consists of equipment wash water and rainfall collected from diked areas around the plant; consequently, the flow rate and composition of the wastewater is cyclical and dependent upon the amount of rain. Plant personnel indicated in September 1986[1] that the steam stripper operated roughly 75 percent of the time. Wastewater accumulates in a storage tank when the stripper is not operating[1]. Once the stripper is started, it operates continuously until the wastewater in storage has been steam stripped.

A flow schematic of the treatment system[1] is given in Figure 1. (Figure 1 is a simplified block diagram because the more detailed process schematic was considered to be confidential business information.) The wastewater enters one of two decanters (each approximately 20,000 gal capacity) where it is processed as a batch. Sodium hydroxide solution (caustic) is added to the decanter to adjust the pH and flocculants are added to aid in solids removal. The mixture is recirculated and mixed in the decanter and allowed to settle. The wastewater (upper layer) is sent to the stripper feed (or storage) tank (approximately 125,000 gal capacity). The organic layer (at the bottom) is removed from the decanter and sent to a surge or collection tank, and solids are periodically removed and dried in a vacuum dryer. The vapors from the dryer are collected in a carbon bed adsorber unit.

The steam stripper is started after a sufficient quantity of water has accumulated in the storage tank. The stripper feed passes through a heat exchanger for preheating by the effluent from the stripper. The stripper column is packed with 1-inch saddles and processes about 12 gal/min. The stripper effluent, after cooling by the heat exchanger, enters one of two open-topped holding tanks (about 5,000 gal) where it is analyzed for comparison with the discharge limits. If the analysis is satisfactory, the water is pumped to a surge tank where the pH is adjusted for final discharge

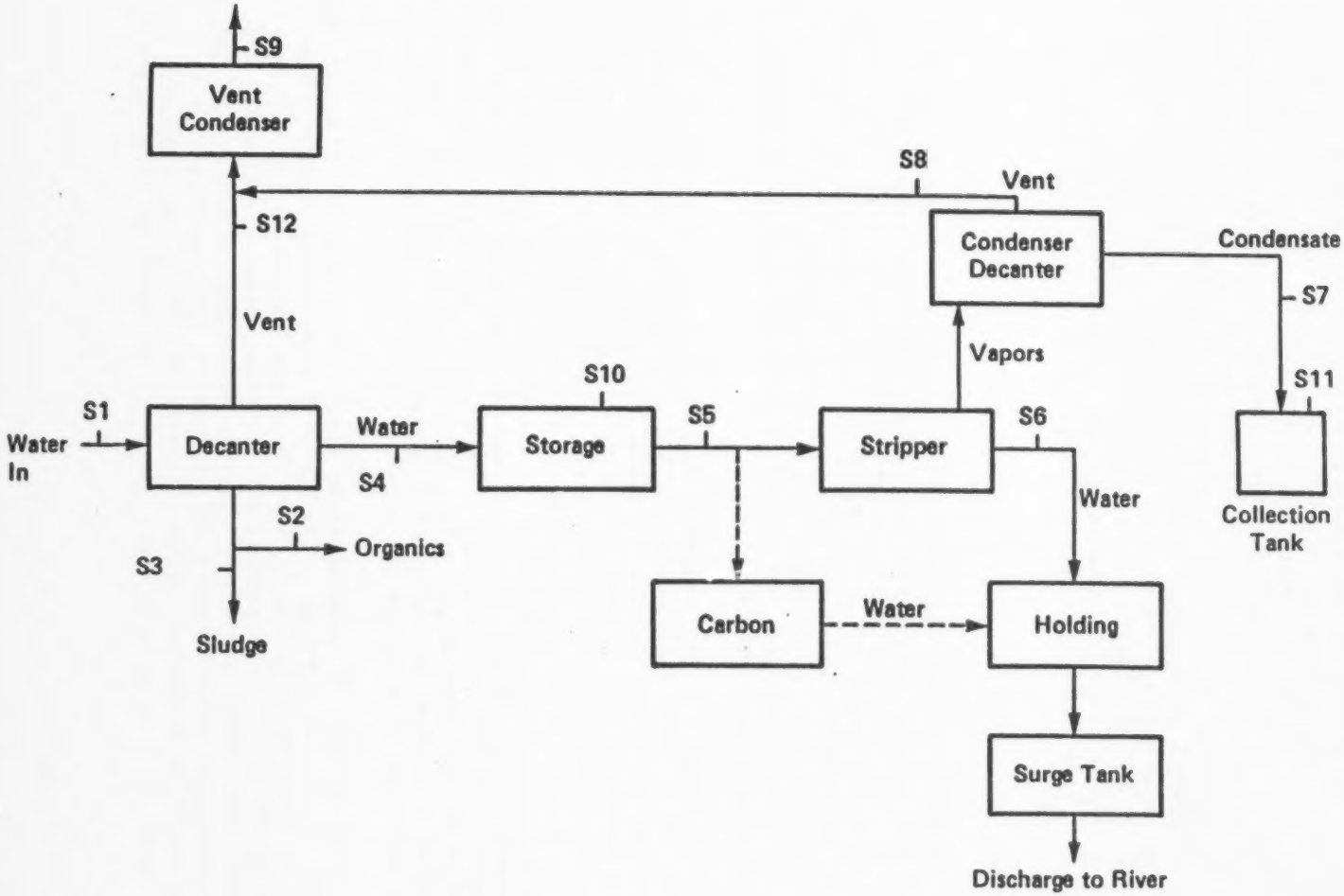

Figure 1. Simplified schematic of sampling points.

(S1, S2, ... S12 indicate sampling locations during 9/86 sampling study by RTI)

to the river under the NPDES permit. Additional pH adjustments can be made at the surge tank and final analyses of the water can be performed before discharge to the river.

The overhead vapors from the stripper pass through a condenser cooled with cooling tower water. The condensate enters a decanter that separates the heavier organic layer from water. The entire water layer is returned to the steam stripper and the organic layer is drained periodically by the operator to a small collection tank for recycle back to the process. The collection tank is open-topped and has a layer of water and sludge floating on top of the organic layer.

The condenser is vented through the decanter to a vent condenser as shown in Figure 1. The vent condenser is now equipped with a refrigeration system with glycol coolant available at -10°C. Although equipped, the condenser is not yet run continuously at the lower operating temperature.[2] The vent condenser receives vapors from the initial water/organics/solids decanters and the steam stripper condenser/decanter. The initial decanters and storage tank are fixed roof tanks and have conservation vents that open as necessary to prevent pressure buildup.

3.0 ESTIMATE OF UNCONTROLLED VOC AIR EMISSIONS

The primary VOC air emission points at the above wastewater treatment facility are the secondary (vent) condenser outlet and the conservation vents on decanter and feedwater storage tanks which open whenever liquid is pumped into these tanks (streams S9, S10, and S12 in Figure 1). The concentration of the volatile C_1-chlorinated solvents in the various vent emission streams were measured in the detailed sampling study conducted by RTI in September 1986,[1] and are given in Table 1.

The measured concentrations of organics at the outlet from primary and secondary condensers are very similar in Table 1 because at the time of this sampling study, the secondary condenser operated at a temperature similar to that of the primary condenser, resulting in very little additional condensation. The secondary condenser is now equipped to use refrigerated glycol as coolant instead of plant cooling water.[2] This modification will allow the condenser to cool the vent gases down to -5°C when fully operational. For the purpose of estimating uncontrolled emissions, the measured concentrations (at the secondary condenser outlet as well as at other vent streams) will be used and the effect of refrigerated glycol cooling will be considered as one VOC control option.

The vent streams are also nearly saturated with water vapor at the respective stream temperatures due to the extended contact with the aqueous phase. Because of the immiscibility of water with the organics phase, the partial pressure exerted by water vapor will be close to the saturated vapor pressure. The balance of the vent stream flows is composed of air.

During the September 1986 RTI sampling study,[1] typical operating conditions for the steam stripper and primary condenser were established. The feed rate to the stripper was about 10.8 gal/min (40.9 l/min) and the

TABLE 1. COMPOSITION OF VENT STREAMS AS MEASURED BY RTI DURING 9/86 SAMPLING STUDY.

Stream	Description	Concentration, Mole %			
		CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
S8	Primary Condenser Vent	0.57	39.18	4.16	0.21
S9	Secondary Condenser Vent	0.53	38.59	4.28	0.29
S10	Storage Tank Vent	0.19	11.04	2.86	0.76
S11	Organics Collection Tank Vent	0.0051	1.81	0.35	0.032
S12	Solids Decanter Vent	0.77	28.57	7.06	2.62

corresponding average primary condenser vent flow was measured to be about 15.06 gal/min (57 l/min) at standard conditions. The secondary condenser outlet flow, however, was measured to be about 3.17 gal/min (12 standard l/min) average. The primary condenser outlet flow rate was measured by venting the outlet directly to atmosphere. In actual operation, the vapors leaving the primary condenser travel through long piping to secondary condenser, causing a significant back pressure (~ 1.5 psig) at the primary condenser. Also the primary condenser outlet vapors are in direct contact with the liquid in the collection tank. Thus during flow measurement at the primary condenser some of the liquid in the collection tank may also have been flash vaporized causing additional flow. Due to the uncertainties involved in the primary condenser flow measurement and almost identical composition of primary and secondary condenser outlet streams (indicating almost no additional condensation in the secondary condenser) the flow rate leaving the primary condenser is assumed to be the same as measured flow at the secondary condenser; i.e., 3.17 gal/min (12 l/min) for a steam stripper feed rate of 10.8 gpm (40.9 l/min).

Attempts to measure the vent flows from the decanter tank and storage tank with the liquid pumping into the tanks failed during the previous sampling study because of opening of conservation vents. The conservation vents are designed to keep the headspace pressure in the tanks within 0.188 - 0.25 psi of atmospheric pressure. Thus the rapid filling of liquid, as currently practiced, forces the conservation vents to open releasing the vapors to atmosphere. The vent flows from these tanks may simply be assumed to be equal to liquid feed rate because of volumetric displacement of the gas with incoming liquid. The total amount and rate of tank vent gases displaced is thus equal to the total volume and rate of the liquid feed in the decanter and storage tanks.

The relatively low vapor phase concentration at S11 and low working losses from the low rate of condensate generation suggest that the air emissions from the organics collection tank would be much lower than the other sources; e.g., for the 10.8 gpm stripper feed rate the rate of primary condensate is about 0.08 gal/min (0.3 l/min), as compared to 3.17 gal/min (12 l/min) primary condenser vent flow rate. Furthermore, the concentration of organics in the collection tank headspace is 2.2% as compared to 44.1% in the condenser outlet vapors. Thus, VOC emissions from S11 may be expected to be only about 0.1% of the primary condenser outlet emissions. Therefore, these emissions will be ignored in the present study.

Recent inquiries with Occidental Chemical Plant personnel[2] indicated that the total amount of the wastewater processed average to about 6.5 gpm for 24 hrs/day, 365 days/yr operation. Thus the total amount of wastewater processed in one year $\simeq 3.4164 \times 10^6$ gallons ($\simeq 12.93 \times 10^6$ liters). Since the total amount of wastewater is fed into decanter tanks and subsequently to feedwater storage tank and then to steam stripper, the total amount of vent flows from each of the major sources may be estimated for the above given total annual wastewater flow. The individual organic compound annual emissions may be determined using their measured concentration given in Table 1:

1) Decanter Tank Vent, S12:	12.93×10^6 liters/year @ 25°C	
Methyl Chloride	$\sim 2.056 \times 10^5$ gm/yr	$\sim$ 452.9 lb/yr
Methylene Chloride	$\sim 1.284 \times 10^7$ gm/yr	$\sim 2.829 \times 10^4$ lb/yr
Chloroform	$\sim 4.462 \times 10^6$ gm/yr	$\sim 9.827 \times 10^3$ lb/yr
Carbon Tetrachloride	$\sim 2.134 \times 10^6$ gm/yr	$\sim 4.700 \times 10^3$ lb/yr
Total	1.964×10^7 **gm/yr**	$\sim$ **4.326 x 10^4 lb/yr**
2) Storage Tank Vent, S10:	12.93×10^6 liters/year @ 25°C	
Methyl Chloride	$\sim 5.074 \times 10^4$ gm/yr	$\sim$ 111.77 lb/yr
Methylene Chloride	$\sim 4.963 \times 10^6$ gm/yr	$\sim 1.093 \times 10^4$ lb/yr
Chloroform	$\sim 1.807 \times 10^6$ gm/yr	$\sim 3.981 \times 10^3$ lb/yr
Carbon Tetrachloride	$\sim 6.189 \times 10^5$ gm/yr	$\sim 1.363 \times 10^3$ lb/yr
Total	7.440×10^6 **gm/yr**	$\sim$ **1.639 x 10^4 lb/yr**
3) Primary Condenser Outlet Stream, S8:	3.796×10^6 liters/year @ 0°C	
Methyl Chloride	$\sim 4.878 \times 10^4$ gm/yr	$\sim$ 107.45 lb/yr
Methylene Chloride	$\sim 5.644 \times 10^6$ gm/yr	$\sim 1.243 \times 10^4$ lb/yr
Chloroform	$\sim 8.424 \times 10^5$ gm/yr	$\sim 1.856 \times 10^3$ lb/yr
Carbon Tetrachloride	$\sim 5.480 \times 10^4$ gm/yr	$\sim$ 120.7 lb/yr
Total	6.590×10^6 **gm/yr**	$\sim$ **1.452 x 10^4 lb/yr**

The total uncontrolled VOC emissions from all 3 sources is thus calculated to be about 33.67 Mg/yr, 74,163 lbs/yr.

Another important aspect from control standpoint is the rate of emissions. The rate of primary condenser outlet vapors is 12 standard l/min when the stripper is in operation, which would roughly be 60% of the time given the normal stripper feed rate and average wastewater generation rate. In the September 1986 study, the stripper operation time was estimated to be about 75% of the time[1]. The reduction from 75% to 60% may be perhaps because of reduced wastewater generation rate due to recent plant modifications. Since the stream concentration used in estimation were the same as those used in the September 1986 study, the reduced wastewater generation rate resulted in a lower estimate of 33.7 Mg/yr VOC emissions as compared to 44 Mg/yr estimate[1] in the previous sampling study report. The normal pumping rates as provided by plant personnel during RTI's recent visit[2] are: 48 gpm for wastewater feed into decanters and 120-140 gpm for liquid feed from decanters to feedwater tank. Thus liquid feed operation into decanters is carried out over only 13.5% of total time and the liquid pumping into feedwater tank occurs only 5% of the time.

4.0 EMISSION REDUCTION MEASURES

The emissions from the feedwater storage tank result when liquid is pumped from the decanter tank to the feedwater tank. Due to the high rate of liquid pumping the conservation vent opens letting out the emissions. At present the feedwater tank headspace is not connected to the decanter tank headspace. The vapor emissions from feedwater tank may be prevented by simply connecting the feedwater tank headspace to the decanter tank head space by a duct. This will allow the displaced vapors to enter the decanter tank during liquid pumping operation. The duct should be of large enough size to handle 130 gpm or 17.4 ft^3/min (492.1 l/min) flow rate with minimal pressure drop (<5 inches of water ~ 0.2 psi) to prevent opening of the conservation vent. This simple ducting arrangement will eliminate 7.44 Mg/yr (16,402 lbs/yr) VOC emissions from the feedwater storage tank, and the total VOC load on a control system will be reduced to 26.23 Mg/yr or 57.753 lbs/yr. Recent discussion with plant personnel[2] indicated that this duct installation will cost up to $3,000 including materials and labor.

In order for any control system to be effective all the vent emission must pass through the control system. Thus a forced drive system downstream of a control system is essential to prevent opening of conservation vents on the decanter and feedwater tanks. The fan or blower must automatically be turned on whenever any liquid pumping operation starts or the steam stripper is running. The vent flow rate from primary condenser is typically 12 standard l/min. which will be present 60% of the time. The maximum flow rate that the drive system would need to be able to handle is 12 standard l/min + 182 lit/min (48 gal/min) from the decanter tank or about 194 l/min (7 ACFM) total. Thus the fan must be able to deliver 7 ACFM of maximum flow in order to prevent pressure buildup in the decanter and feedwater tanks during liquid filling operations and consequently to prevent opening of conservation vents. The fan should also be able to reduce the flow to 12 l/min when only the steam stripper is in operation to prevent excessive vacuum in the decanter and feedwater tanks. Due to the variability of the total vent emission flow rate, the fan should be of flexible capacity from 10 to 200 l/min (0.3 to 7.5 ACFM) and its operating capacity should be controlled by the wastewater treatment operation.

Also it is very important to prevent any unwarranted emissions such as those occuring through overflow vents for liquid level. During RTI's earlier sampling trip,[1] it was found that vapors from the decanter tanks were discharging at ground level through pipes installed as overflow lines connected near the top of the tanks. These lines were plugged for RTI's sampling and were reported to plant personnel for modification such as installation of traps on decanter tank overflow plumbing. No vent control system will operate properly when vent gases discharge through uncontrolled exits. This problem was reidentified to current plant personnel during RTI's most recent sampling trip[2], for proper modifications.

5.0 EVALUATION OF CONTROL OPTIONS

The emission of volatile organics from the steam stripper plant may be reduced by condensing the organics at a lower temperature or by using a carbon adsorption system. A combination of both approaches is also possible. The secondary vent condenser at Occidental's wastewater treatment plant is now

equipped to use refrigerated glycol at -5 to -10°C as coolant. This lower operating temperature as compared to primary condenser would allow additional organics to condense thereby reducing their emissions. Carbon adsorption systems have been shown to be very effective for removing chlorinated organics.[3] The Occidental plant uses such a carbon adsorption system to treat sludge dryer emissions. The dryer vapor emissions are thus reported to be reduced by more than 99%.[2]

5.1 Refrigeration System Using Glycol

5.1.1 Exit Gas Temperature = -5°C

The refrigerated glycol is available at -5 to -10°C. Thus it may be assumed that the vent gases can be cooled only down to -5°C. Because of the intermittent nature of the two primary emission sources and difference in the stream compositions, the condenser performance can change with time. Looking at the estimate of total emissions, almost 75% of the total VOC emissions come from decanter tank vent. The maximum load that the condenser will experience may be determined by assuming that the liquid is pumped into the decanters while the steam stripper operates. The total maximum vent flow rate at such conditions would be ~ 194 l/min with a composite composition of S8 and S12 stream as follows:

CH_3Cl	0.76 mol%
CH_2Cl_2	29.23 mol%
$CHCl_3$	6.88 mol%
CCl_4	2.47 mol%
Inerts + Water	60.66 mol%

The stream may also be assumed to be saturated with water vapor at the primary condenser exit temperature of 21°C. Since water is immiscible with organics phase, its concentration in the vent gases would be 2.45 mol%, corresponding to the saturated vapor pressure.

For the above feed composition and for condenser exit vapor temperature of -5°C, the amount of vapor that would be condensed may be calculated from equilibrium considerations as shown in Table 2. The calculations take into account the immiscibility of the water and organic phases and uses Raoult's law to calculate equilibrium vapor pressure of each organic component. The computation for vapor exit temperature of -5°C indicate that almost 77.7% of the organic vapors may be condensed in the secondary condenser.

Applying individual condensation efficiencies for each component total organic vapor emissions after condensation may be estimated:

Methyl Chloride	~ 2.099×10^5 gm/yr ~ 462.3	lb/yr
Methylene Chloride	~ 4.542×10^6 gm/yr ~ 10,000	lb/yr
Chloroform	~ 6.217×10^5 gm/yr ~ 1,369	lb/yr
Carbon Tetrachloride	~ 1.499×10^5 gm/yr ~ 330.2	lb/yr
Total VOC Emissions	**5.524 Mg/yr ~ 12,166**	**lb/yr**

In terms of VOC mass emission, the secondary condenser operated at gas exit temperature of -5°C would reduce mass emission by 78.9% to 5.52 Mg/yr.

TABLE 2. DETERMINATION OF EXIT GAS COMPOSITION AND AMOUNT OF VAPORS CONDENSED.

Basis: 1 gmole of Feed Vapor
Exit Gas Temperature = -5°C

Feed Gas Component	Moles in Feed Gas	% of Feed Condensed	Moles Condensed	n_i Moles in Gas	X_i Organic Phase Mole Function	K_i Relative Volatility	K_iX_i Equilibrium Gas Phase Mole Fraction	$Y_i = n_i/\Sigma n_i$ Gas Phase Mol Fraction
CH_3Cl	0.0076	17.49	0.001329	0.00627	0.004350	2.1434	0.009324	0.009321
CH_2Cl_2	0.2923	75.43	0.2205	0.07182	0.721576	0.14792	0.106735	0.106753
$CHCl_3$	0.0688	88.28	0.06074	0.00806	0.198774	0.06030	0.011986	0.011985
CCl_4	0.0247	93.15	0.0230	0.00169	0.075299	0.03339	0.002514	0.002514
H_2O	0.0245			0.0028				0.004162
Inert	0.5821			0.5821				0.865265
			0.30556	0.67274				1.0

5.1.2 Exit Gas Temperature = 2°C

Because of the intermittent nature of emissions one potential problem in keeping condenser exit gas temperature below 0°C is icing. Whenever vapor flow to condenser stops, ambient humidity can easily enter the condenser and cause icing blockage problems. One way to prevent icing is to keep the exit gas temperature above 0°C. Therefore, condensation equilibrium calculation were also carried out for exit gas temperature of 2°C, as shown in Table 3. Because of the higher exit gas temperature, the condensation of organics would be decreased to about 67.4%. By applying individual condensation efficiencies for each component, the total organic vapor emissions after condensation at 2°C may be estimated:

Methyl Chloride	~ 2.241×10^5 gm/yr ~ 493.7 lb/yr
Methylene Chloride	~ 6.669×10^6 gm/yr ~ 14,696 lb/yr
Chloroform	~ 1.012×10^6 gm/yr ~ 2,229 lb/yr
Carbon Tetrachloride	~ 2.559×10^5 gm/yr ~ 563.6 lb/yr
Total VOC Emissions	**8.161 Mg/yr ~ 17,976 lb/yr**

The reduction in VOC mass emission in this case would be 68.9%, with emissions of 8.16 Mg/yr.

5.1.3 Energy Balance

The existing secondary vent condenser consists of eight (8) 3/4" ID and 10' long tubes. In order to determine the ability of this condenser to handle all of the vent vapor emissions load, an energy balance was carried out. Since the gas cooling to -5°C involves maximum condenser duty with minimum temperature driving force, the exit gas temperature was assumed to be -5°C in energy balance calculations.

Basis (mass balance): 1 gmole of feed gas to condenser @ 25°C

Basis (energy balance): Enthalpy of liquid phase = 0 @ -5°C

Assume that gases are cooled down to -5°C at exit. The physical properties of each component in the gas phase are given in Table 4. The mole fraction of each component in the feed and exit gases as well as moles of liquid condensed are given in Table 2.

Enthalpy of condensate liquid out = 0

Enthalpy of exit gases (as given by latent heat):

CH_3Cl :	0.00627 x 4934.36	= 30.94 cal
CH_2Cl_2 :	0.071818 x 7232.12	= 519.40 cal
$CHCl_3$:	0.008063 x 7791.77	= 62.83 cal
CCl_4 :	0.001691 x 8070.58	= 13.65 cal
H_2O :	0.0028 x 10991.48	= 30.78 cal
Air :	Latent heat ignored	= 0
Total Enthalpy of Exit Gases		**= 657.60 cal**

TABLE 3. DETERMINATION OF EXIT GAS COMPOSITION AND AMOUNT OF VAPORS CONDENSED.

Basis: 1 gmole of Feed Vapor
Exit Gas Temperature = 2°C

Feed Gas Component	Moles in Feed Gas	% of Feed Condensed	Moles Condensed	n_i Moles in Gas	X_i Organic Phase Mole Function	K_i Relative Volatility	K_iX_i Equilibrium Gas Phase Mole Fraction	$Y_i = n_i/\Sigma n_i$ Gas Phase Mol Fraction
CH_3Cl	0.0076	11.89	0.000903	0.00669	0.003407	2.7486	0.009364	0.009361
CH_2Cl_2	0.2923	63.92	0.186838	0.10546	0.704445	0.2093	0.14744	0.147442
$CHCl_3$	0.0688	80.92	0.055672	0.01313	0.209906	0.08742	0.01835	0.018352
CCl_4	0.0247	88.31	0.021812	0.00289	0.082241	0.04912	0.004039	0.004036
H_2O	0.0245			0.0050				0.00699
Inert	0.5821			0.5821				0.81382
			0.265227	0.71527				

TABLE 4. PHYSICAL PROPERTIES

Component	Heat of Vaporization @ -5°C cal/gmole	Gas Phase Specific Heat (-5° to 25°C) cal/gmole °K
CH_3Cl	4934.36	9.44
CH_2Cl_2	7232.12	11.81
$CHCl_3$	7791.77	15.37
CCl_4	8070.58	19.71
H_2O	10,991.48	8.014
Air	--	6.902

Enthalpy of gases entering condenser (as given by latent and sensible heat):

CH_3Cl	:	0.0076 x (4934.36 + 9.44 x 30)	= 39.65 cal
CH_2Cl_2	:	0.2923 x (7232.12 + 11.81 x 30)	= 2217.51 cal
$CHCl_3$	:	0.0688 x (7791.77 + 15.37 x 30)	= 567.80 cal
CCl_4	:	0.0247 x (8070.58 + 19.71 x 30)	= 213.95 cal
H_2O	:	0.0245 x (10991.48 + 8.014 x 30)	= 275.18 cal
Air	:	0.5821 x (6.902 x 30)	= 120.53 cal
		Total Enthalpy of Feed Gas	**= 3434.62 cal**

Therefore, energy removed in the condenser = 2777 cal/gmole feed gas.

Maximum flow rate of feed gas = 194 l/min @ 25°C ≡ 7.93 gmoles/min.

Thus maximum condenser heat duty = 7.93 x 2777.02
= 2.202×10^4 cal/min
= 87.39 Btu/min
≡ **0.44 ton of refrigeration**

Existing secondary condenser inside surface area = π x (0.75/12) x 8 x 10
= 15.71 ft^2

Assuming glycol temperature of -6°C on cooling liquid side, the log mean temperature gradient = 8.74°C. Therefore, to achieve, the maximum required condenser duty the overall heat transfer coefficient required

= 87.39 x 60 / (15.71 x 8.74 x 1.8)
= 21.2 Btu/hr-ft^2-°F

Since the typical value for overall heat transfer coefficient for condensers is usually between 40 - 100 Btu/hr-ft^2-°F, the existing condenser may be expected to satisfactorily handle the maximum condensation load.

5.1.4 Cost Estimate for Refrigerated Cooling

Since the secondary condenser is already in place and equipped for glycol cooling, no additional capital cost is required. The maximum heat duty required is only 0.44 tons of refrigeration. According to the plant personnel[2] 10-15 tons of refrigeration capacity is currently available at the plant site with an operating cost of $1000/ton/year.

Thus the operating costs associated with glycol cooling would be less than $500/year. In addition, operator/maintenance labor cost may be considered as ~ $1,825/yr, @ 0.5 hr/day and $10/hr. The total operating costs may thus be calculated to be about $2,325/yr.

5.1.4.1 Recovery Credits

With a condenser operating temperature of -5°C almost 45,580 lbs of organics will be recovered per year. The corresponding recovery credit will be $5,700/yr @ $0.125/lb of organics recovered.

For higher condenser operating temperature of 2°C about 39,780 lb of organics will be recovered resulting in $4,970 recovery credit @ $0.125/lb of organics recovered.

5.2 Carbon Adsorption System

Since the maximum expected vent flow rate is only 194 l/min (~ 7 ft^3/min) the design of carbon adsorption system will simply be based on the desired capacity. The activated carbon may generally be expected to be very efficient for higher chlorinated hydrocarbons.[3] The adsorption capacity of activated carbon for methyl chloride under dry conditions is about 0.03 lb/ lb carbon, whereas for methylene chloride, chloroform and carbon tetrachloride the capacity under dry conditions is about 0.5 lb/lb carbon according to one vendor.[3] The low capacity for methyl chloride will not be a significant problem in the present case due to its low gas phase concentration compared to methylene chloride. For humid saturated conditions the dry capacities may be reduced[3] by 60 - 70%, i.e., the reduced capacity would be 0.02 lb/lb carbon for methyl chloride and 0.35 lb/lb carbon for the other organics. The removal efficiency for all organics is expected to be greater than 99% for inlet vapor concentrations in the percentage ranges. Methyl chloride is likely to be the first compound to break through due to its low capacity for adsorption.

For a system employing parallel beds with alternate adsorption and steam regeneration, the working capacity may be expected to be reduced as compared to fresh carbon capacity. Due to the low boiling compounds, the working capacity is likely to be reduced by only 5% according to one vendor.[3] For a conservative estimate, a 50% reduction in the capacity will be assumed in the present case. Thus the capacity of carbon under water saturated conditions may be considered to be 0.01 lb/lb carbon for methyl chloride and 0.17 lb/lb carbon for other organics.

The total emission of uncontrolled organics as estimated in sections 3.0 and 4.0 is about 57,800 lb/year or about 158.4 lb/day. For a one-day adsorption/regeneration cycle, the amount of carbon required in the adsorption bed using capacity for higher hydrocarbons is 932 lbs. Due to low concentration of methyl chloride, this amount of carbon will have an adequate capacity to adsorb all of methyl chloride as well.

For design consideration, two parallel beds holding 1000 lb of activated carbon each may be assumed. With a typical carbon bulk density[3,4] of about 30 lb/ft^3, the volume of the carbon bed is calculated to be 33.33 ft^3. A 3.5' dia, 6.5' tall vessel with an internal volume of 62.8 ft^3 will be adequate to house 1000 lbs of carbon. Steam stripping of an exhausted bed followed by condensation may be expected to recover almost 90% of the organics. The vent stream flow from the adsorber/condenser may be added into the total vent stream of the wastewater treatment plant to be processed again. Condensate liquid may be decanted into organic and aqueous fractions. The organic

fraction may be recycled to the process along with the organic condensate from primary and secondary condensers. The aqueous stream can be sent back to the wastewater treatment system, making all streams integrated to the existing wastewater treatment plant.

With a 99+% removal efficiency in the adsorber the organic emissions will be reduced to 580 lb/year or less. Since the wastewater treatment system is of intermittent nature, the carbon adsorption beds must be equipped with a VOC detector at the outlet to signal breakthrough and need for regeneration.

5.2.1 Cost Estimate

5.2.1.1 Estimated Capital Costs

The capital and operating costs associated with the carbon adsorption system may be estimated using the guidelines provided in the EAB Control Cost Manual.[5]

Initial Carbon, 2000 lbs @ $2/lb of fresh carbon	$ 4,000
2 Adsorber Vessels (3.5' diameter, 6.5' tall)	15,000
Fan, pumps, decanter, condenser, internal piping [0.39 (4,000 + 15,000)]	7,400
Adsorber equipment total cost	**$26,400**
Instrumentation, taxes, freight, (0.18 x 26,400)	4,750
Total purchased equipment	**$31,150**
Installation Cost (~30%) (foundation, supports, erection, electrical, piping, insulation, etc.)	9,350
Indirect cost (~31%) (engineering, supervision, construction and field expenses, construction fee, startup, etc.)	9,650
Cost of ductwork[2] to bring vent gases from secondary vent condenser outlet to adsorber system (including installation)	5,000
Total Capital Investment	**$55,150**

5.2.1.2 Estimated Operating Costs

i)	Steam Cost: steam consumption @ 3.5 lb/lb adsorbed VOC ~ 2.023 x 10^5 lb/yr	
	Steam cost @ \$5/1000 lb	\$1,000/yr
ii)	Cooling water cost: (same as steam cost)	1,000/yr
iii)	Electricity (very little pressure drop across bed due to low flow)	200/yr
iv)	Carbon replacement (for 5-year carbon life) 0.2638 (1.08 x 4000) + 250	1,200/yr
v)	Indirect annual cost [50,150 - (1.08 x 4000 +250)] x 0.1628	7,420
vi)	Operating and maintenance labor (1 hr/day @ \$10/hr)	3,650/yr
	Total Annual Operating Costs	**\$14,470**
	Possible Recovery credit (with a 90% recovery, rate about 52,020 lb of organics will be recovered every year resulting in \$6500 recovery credit @ \$0.125/lb) of recovered organics)	**\$ 6,500/yr**

5.3 Combined Refrigeration and Carbon Adsorption System

In this option, a carbon adsorption system will be installed downstream of the secondary vent condenser to take advantage of the existing secondary condenser facility and to reduce load on the carbon adsorption system. Because of the icing problems associated with lower operating temperature of -5°C, the condenser is assumed to operate at a temperature of 2°C. From section 5.1.2, the resultant organic loading on the carbon adsorption system would be about 18,000 lb/year, or about 49.3 lb/day.

The secondary condenser also will reduce the amount of water vapor in the gas stream considerably increasing the adsorption capacity of the activated carbon. Assuming a conservative 50% reduction in the carbon capacity due to regeneration, the capacity of the activated carbon may be assumed to be 0.25 lb/lb carbon. The amount of carbon required for one day cycle is therefore about 200 lb/day. The corresponding volume of carbon would be 6.67 ft^3. A vessel of 2' diameter and 4' depth with an internal volume of 12.6 ft^3 will be able to house 200 lbs of activated carbon.

Due to low concentration of methyl chloride, this amount of carbon will have an adequate capacity for adsorbing all of the methyl chloride as well.

With 99+% removal efficiency for organics, their emission may be expected to be reduced to 180 lb/year or less. Again, due to the intermittent nature of the wastewater treatment system, the carbon adsorption beds must be equipped with a VOC sensor at the outlet to signal VOC breakthrough and need for regeneration.

Because of the intermittent nature of the wastewater treatment system, it may also be possible to use a single larger bed of carbon and regenerate it every 4 to 5 days whenever steam stripper and liquid filling operation are not in progress. For example, a single bed of 1000 lb carbon as discussed in section 5.2 will be able to provide enough carbon for 5 days. However, an adsorption system with two smaller beds may be preferable as it will not put any constraints on the main wastewater treatment plant.

5.3.1 Cost Estimate

A two-bed system with each holding 200 lb of carbon is considered for cost estimation. The capital and operating costs are based on the EAB Control Cost Manual guidelines.[5]

5.3.1.1 Capital Costs

Capital costs may be determined using rule of scale and the cost of the larger system discussed in 5.2. Using a scaling factor[6] of 0.6, the capital cost for the adsorption system may be estimated to be:

~ $50,150 $(1/5)^{0.6}$	~ $19,100
Cost of ductwork[2] to bring vent gases from secondary vent condenser outlet to adsorber system (including installation)	5,000
Total Capital Investment	**$24,100**

5.3.1.2 Estimated Operating Costs

i)	Steam cost: @ 3.5 lb/lb of adsorbed VOC and $5/1000 lb steam	$ 340/yr
ii)	Cooling water cost	340/yr
iii)	Electricity	200/yr
iv)	Carbon replacement for 5-year carbon life: 0.268 (1.08 x 800 + 250)	300/yr
v)	Indirect annual cost for carbon adsorption system [19,100 - (1.08 x 800 + 250)] x 0.1628	2,930/yr
vi)	Glycol refrigeration cost (section 5.1.4)	500/yr

vii) Operating and maintenance labor 5,474/yr
(1.0 hr/day @ $10/hr) - Adsorption sys.
(0.5 hr/day @ $10/hr) - Refrigeration sys.

Total Operating Costs **$10,085/yr**

Possible Recovery Credit:

Secondary Condenser System (sec. 5.1.4.1) 4,970/yr

Adsorption System 2,030/yr
(With a 90% recovery rate, about 16,200 lbs of organics will be recovered every year by the adsorption system resulting in $2,025 credit @ $0.125/lb

Total Recovery Credit **$7,000/yr**

5.4 Summary

The estimates for cost, emission of organics and recovery of organics for each option are summarized in Table 5. Due to the limited time available for this study, no optimization of the control systems is made, e.g. adsorption cycle time. The costs presented are therefore rough estimates for preliminary assessment. As seen from this table, use of secondary vent condenser with refrigerated glycol cooling followed by carbon adsorption offers the lowest cost for high organics removal efficiency. The refrigerated cooling alone provides the best ratio of organics removed per total cost, however, it will still result in significant organic emissions of 12,000 to 18,000 lbs/year.

6.0 CONCLUSIONS

Based upon this study, the following conclusions may be drawn for efficient organics removal from wastewater treatment system vent VOC emissions at the Occidental Chemical Plant at Belle, West Virginia.

1. Connecting the headspaces of storage feedwater tank and decanter tanks will eliminate the source of VOC vent emissions (working losses) at the feedwater tank. This will result in 7.44 Mg/yr reduction in VOC emissions.

2. For any control system to be effective, a forced drive system such as a fan or blower at the downstream of the control system is essential to carry the vent gases through the system and to prevent opening of the conservation vents. Moreover, the fan should be of flexible capacity controlled by wastewater treatment operations. For example, whenever liquid is being filled in the decanter tank, the fan must pull vent streams at the same rate as liquid pumping rate; and when only the steam stripper is running the fan must reduce the vent flow rate accordingly so as not to cause any vacuum in the storage or decanter tanks.

TABLE 5. COMPARISON OF THREE CONTROL OPTIONS.

Option #	Description	Amount of Organics Removed (lbs/yr)	VOC Emissions (lbs/yr)	Total Capital Cost, $	Annual Operating Costs, $/yr	Possible Recovery Credit, $/yr
1	Refrigerated cooling at -5°C*	45,590	12,160	--	2,325	5,700
1A	Refrigerated cooling at 2°C	39,750	17,980	--	2,325	4,970
2	Carbon adsorption alone	57,170	580	55,150	14,470	6,500
3	Refrigerated cooling at 2°C followed by carbon adsorption	57,570	180	24,100	10,090	7,000

* Possibility of icing blockage problems

3. It is necessary to prevent any unwarranted vapor emissions such as those occurring through overflow vents for liquid level (e.g., decanter tank overflow plumbing) by installing liquid traps.

4. The secondary vent condenser is capable of condensing up to 68% by mass of vapors in the feed stream using refrigerated glycol cooling operated at the gas exit temperature of 2°C. This will result in recovery of 18.07 Mg/yr of organics with annual VOC emissions of 8.16 Mg/yr.

5. A combination of the refrigerated glycol cooled secondary condenser and a subsequent carbon adsorption system will be able to remove almost all of the organics in the vent emissions at a lower cost than that for a carbon adsorption system alone. The value of recovered organics will be able to pay for almost 70% of the total operating costs. The VOC emissions may be expected to be reduced to 180 lbs/yr.

7.0 REFERENCES

1. Branscome, M., S. Harkins, and K. Leese, "Field Test and Evaluation of the Steam-Stripping Process at Occidental Chemical, Belle, WV", Research Triangle Institute Project Report prepared for Hazardous Waste Engineering Research Laboratory, U.S. EPA Contract No. 68-03-3253, Work Assignment 1-6, March 1987.

2. Harkins, S. Report to EPA/OAQPS of trip to Occidental Chemical Plant, Belle, WV, September 1988. (Attached as an Appendix to this report).

3. Roy, Al, Calgon Corporation, Technical Representative, personal communication, August 1988.

4. Spivey, J.J., "Recovery of Volatile Organics from Small Industrial Sources", Environmental Progress, Vol. 7, No. 1, pp. 31-40, February 1988.

5. Vatavuk, W.M., W.L. Klotz and R.L. Stallings, "Carbon Adsorbers" Section 4 in EAB Control Cost Manual, 3rd ed., EPA 450/5-87-001A, February 1987.

6. Peters, M.S. and K.D. Timmerhaus, "Plant Design and Economics for Chemical Engineers", pp. 166-167, McGraw-Hill Bank Company, New York, 1980.

APPENDIX

Report for RTI Trip to Occidental Chemical Plant.

Belle, WV. July 1988

RESEARCH TRIANGLE INSTITUTE

Center for Process Research

James J. Spivey, Ph.D.
Director

September 12, 1988

MEMORANDUM

TO: Robert B. Lucas, EPA/OAQPS

FROM: Scott Harkins, RTI

RE: Report for the Trip to Occidental Chemical Plant, Belle, WV

Purpose

The purpose of this trip was to discuss organic vapor emissions from Occidental's steam stripper and wastewater treatment operations, source of the emissions, and possible control options; and to obtain additional information.

Place

Occidental Chemical Corporation
Electrochemicals Division
Belle Plant
P. O. Box 615
Belle, WV 25015

Attendees

Scott Harkins, RTI

Robert Lucas, EPA-OAQPS

Al Azevedo, West Virginia APCC

Larry Hearn, Occidental

Steve Meadows, Occidental

Post Office Box 12194 Research Triangle Park, North Carolina 27709 Telephone: 919 541-6000

S. Harkins Trip Report to Lucas

On July 1, 1988 Scott Harkins (RTI) and Bob Lucas (EPA/OAQPS) conducted a site visit to the West Virginia Air Pollution Control Commission and the Occidental Chemical Corporation's Plant in Belle W.Va. This visit was to discuss organic vapor emissions from Occidental's steam stripper and wastewater treatment operations, the generation of the emissions, and possible control options. Additional process information was requested to assist in evaluating vapor emissions control options.

Bob Lucas and Scott Harkins initially met with Al Azevedo (West Virginia Air Pollution Control Commission (APCC), 1158 Washington St. East, Charleston, W.Va., 25311, (304) 348-4022) for an hour before proceeding to the Occidental plant. At the Occidental plant Lucas, Harkins, and Azevedo met with Larry Hurn and Steve Meadows (Occidental Chemical Corporation, Electrochemicals Division, Belle Plant, POB 615, Belle, W.Va., 25015, (304) 949-4515). Larry Hurn was the principal contact at the plant. The steam stripper equipment was examined after a discussion (approx. 1 hr) with the plant personnel. Lucas, Harkins, and Azevedo ate lunch after leaving the plant. This was followed by a short meeting at the W.Va APCC offices prior to departure.

Al Azevedo related the APCC's recent involvement with the plant. The W.Va. APCC conducted a risk assessment of air pollutants in the Kanawa valley from the chemical plants in the region. Although the Belle Occidental plant is a relatively small chemical plant the risk assessment indicated its emissions were the most significant risk in the area. The largest source of emissions from the plant was fugitive emissions while the second highest was from the wastewater processing operations. The plant has hired a contractor to check for leaks on a quarterly basis. The discovered leaks are then repaired to reduce fugitive emissions. W.Va. APCC would like the Control Technology Center (CTC) of EPA/OAQPS to assess possible control technology options to minimize emissions of volatile organic chemicals (VOC) from the wastewater treatment facility at Occidental Chemical.

RTI sampled the steam stripper process and vents in September 1986 as part of an EAA-ORD project. The vent emission measurements and estimates of total emissions were used by WVAPCC in the risk assessment for the plant. The vapor emissions reported by RTI were much higher than earlier estimates of vapor emissions from the wastewater treatment system (estimated as 79 lbs of organic vapor/year in the 1984 inventory of the plant site). The organic vapor concentrations in gas above water in the decanter tanks and feedwater tank were much higher than previously believed. The ineffectiveness of the condenser for the decanter tanks (secondary steam stripper condenser) was not identified prior to RTI's sampling of the wastewater treatment process.

Several changes to the wastewater treatment system have occurred since RTI's 9/86 sampling of this process:

1) A sludge drier is currently being installed for the dehydration of decanter tank sludge. This drier is adjacent to the decanter tanks and feed sludge is pumped directly into the drier. The drier operates under a vacuum and two sets of condensers/decanters are placed before and after the vacuum pumps. Gases from the second condenser/decanter (glycol cooled) are passed through two carbon beds (in series) prior to discharge. Used carbon beds will be collected by the activated carbon vendor/supplier and regenerated offsite. The sludge dewatering system (when operated properly) would not significantly increase the vapor emissions from the treatment operations due to the carbon bed VOC control system installed.

2) Another significant change to the system was the conversion of the decanter tank condenser from plant cooling water to refrigerated glycol. The operating temperature of the condenser will be -6 to -8 °C when operational. This will condense much more of the vent gas from the primary steam stripper condenser. It is connected to but will not efficiently condense the vent flows from the decanter tanks during tank filling, as these flows are too high for the condenser and the decanter tank conservation vents will open and vent to the atmosphere.

3) One modification which should have occurred was the installation of traps on decanter tank overflow plumbing. During RTI's earlier sampling trip we found that vapors from the decanter tanks were discharging at ground level through pipes installed as overflow lines connected near the top of the tanks. These lines were plugged for RTI's sampling and were reported to plant personnel for modification. No vent control system will operate properly when vent gases discharge through uncontrolled exits. This problem was reindentified to current plant personnel for proper modification.

4) Several modifications to the plant operating conditions have reduced the volume of wastewater for treatment. Heat exchangers at several locations were changed from steel to titanium. The new heat exchangers require cleaning less frequently and produce less wastewater from the cleaning operations. New gutters were installed on a plant building, routing rainwater to rainwater discharge rather than the wastewater treatment plant. Feed filtering systems for the distillation columns were improved, increasing intervals between cleanings. These changes result in less operation of the wastewater treatment system. Although the above mentioned changes may reduce the total amount and rate of wastewater generation, it may not necessarily reduce the organic vapor concentration in various vent streams as measured in RTI's September 1986 sampling study. Also, since the maximum vent flow rates are determined by liquid pumping rate into the decanter and feedwater tanks and by operating rate of the steam stripper, these flow rates will not be affected by these plant modifications.

There are no current standards for the vent emissions and the control design should remove a large percentage of the methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2) chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). The vent emissions predominantly contain methylene chloride and chloroform and thus the control strategy should focus on these to compounds.

The measurements of vent concentrations and flowrates collected by RTI in 1986 will be used for the control design and calculations of vent emission rates. There are no additional data collected since the last study on the process vent streams to be included in the design. These data were collected in the month of September but will be assumed to be representative of the plant vapor emissions during the entire year.

Additional information provided by Larry Hurn of Occidental Chemical Plant regarding wastewater treatment system operation is given below:

1.	Refrigerated glycol temperature cooling	-5°C minimum
2.	Refrigerated glycol availability at the plant	10-15 tons of refrigeration
3.	Glycol operating costs at the plant	$1000/ton/yr
4.	Steam cost at the plant	$3.75/1000 lbs
5.	Carbon used in the adsorption system on sludge dryer emissions	GAC 8-mesh x 30 mesh from PBS carbon
6.	Carbon cost (fresh)	$2/lb carbon
7.	Offsite carbon regeneration cost	$0.80/lb carbon + freight expenses
8.	Recent changes to steam stripper operation	Upgraded transfer pumps between decanter and feedwater tank
9.	Size of the secondary vent condenser	Shell and tube condenser consists of 8 tubes, 3/4" ID, and 10' long
10.	Current average rate of wastewater treatment	6 to 7 gpm for 24 hr/day 365 day/yr operation
11.	Flow rate into decanter tanks	48 gpm typical (37 gpm wastewater, 11 gpm caustic soda solution). Transfer pumps rated from 25 to 100 gpm, but long pipe length reduces maximum flow rate.

12.	Flow rate from decanter to feedwater tank	120-140 gpm. Pump is rated at 140 gpm.
13.	Distance between decanter tank and storage tank headspaces	~ 25' horizontal, 10' vertical
14.	Approximate cost estimate to connect the top of the decanter to the top of the storage tank	~ $2000 - $3000
15.	Height of decanter tank secondary vent condenser	~ 40'
16.	Length of duct required to bring the gases from secondary vent condenser to the probable location of adsorption system on ground level	~ 150'
17.	Cost to install the duct work to connect condenser outlet stream to adsorber unit	~ $4000 - $5000
18.	Approximate value of recovered and organic condensate in condenser	~ $250 - $300/ton ~ $0.125/lb of organics

RTI will prepare a technical and economic evaluation of control options for the vent stream. Estimated costs and emission reductions will be reported. The designs will be based on the maximum expected vent flow with concentrations based on RTI's previous vent sampling. For all designs the feedwater tank will be vented to a common header with the decanter tanks. When liquid is pumped from the decanter tanks to the feedwater tank the gas displaced from the feedwater tank will flow into the top of the decanter tanks. This vent line will eliminate emissions associated with water transfer from the decanters to the feedwater tank. When water is pumped into the decanters gas from the top of the decanter tanks will be vented through the control system. The control system will also handle the 12 lpm vent stream from the primary steam stripper condenser.

A problem associated with any control system for the tank vents is the tank operating pressure. The decanter tanks and feedwater tank were designed for atmospheric operation. The conservation vents at the top of the tanks open at very small pressure differences from atmospheric pressure. If an installed control system places more than an extremely small back pressure on the vent lines the conservation vents will open and vent displaced gas to the atmosphere. Since these vents are on top of the tanks, operators would probably not notice the discharge. An alarm system to indicate open conservation vents could be installed to show a failure of an installed vent control system.

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